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Compositional Heterogeneity and Molecular Weight Distribution of Copolymer Systems.

3. Heterogeneity of Radial Teleblock Copolymers¹⁾

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A theory of random-coupling of block copolymerization was extended to describe the compositional heterogeneity and molecular weight distribution of mixed radial teleblock copolymers, which are mixture of star-shape block copolymers of $(SB)_fX$ ($f=1, 2, \dots$: number of arms) type. Expressions of gel permeation chromatograms were also derived, incorporating the concepts of the Strasbourg universal calibration and Tung's dispersion correction due to the limited resolution of gel permeation chromatographic columns in addition to the random-coupling theory. The results were compared with experimental chromatograms, and found to be in reasonably good agreement. Then presumably other distributions such as of compositional heterogeneity and molecular weight deduced from the theory are also correct, although there are no adequate techniques of testing such distributions.

INTRODUCTION

Now well-known thermoplastic elastomers²⁾ are linear SB S triblock copolymers, where S is a glassy polymer block such as polystyrene while B is an elastomeric polymer block such as polybutadiene. From these materials a new class of block copolymers have been evolved. They are radial teleblock copolymers³⁾ of $(SB)_fX$ type in which f pieces of SB -block copolymer chains are chemically joined by a coupling agent X through their active B -ends. The spirit is to obtain high molecular weight polymers without increasing bulk viscosity too high: The high molecular weight leads to improvement in the use-properties such as tensile strength and shear resistance, while the relatively low viscosity allows an easy processing of the material. The use-properties depend on their primary structure such as average chemical composition, molecular weight, and number of star branches. However, they should also depend on the heterogeneities. Conceivably in an industrial reactor the product should be contaminated with undesired species such as, in this case, S -homopolymer precursors, SB -diblock intermediates, and teleblock species of fewer branch numbers than desired.

In a previous article (Part 1) of this series⁴⁾ we developed a theory which gives a complete description of average molecular weights (MW s), compositional heterogeneity (CH) and molecular weight distribution (MWD) of multiblock copolymers and of mixture of multiblock copolymer species. To do this we only need to know the MWD s of the precursor homopolymers, block number and relative amount of each species, if it is a mixture. The mixed teleblock copolymers described above are an interesting object of such an

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analysis. We have applied the theory⁴⁾ to facilitate a complete analysis of their heterogeneity. In practical analysis one often uses gel permeation chromatography (*GPC*).⁵⁾ Especially use of a dual detector *GPC* which has refractometric (*RI*) and *UV*-absorption (*UV*) detectors is convenient for characterizing copolymers composed of at least one *UV*-absorbing monomer species.⁶⁾ Therefore, we will attempt to interpret dual detector *GPC* chromatograms in terms of the *CH*- and *MWD*-function of radial teleblock copolymer, employing the Strasbourg universal calibration rule in *GPC*.⁷⁾ Although there has been an increasing tendency of installing in *GPC* more sophisticated detectors such as viscometric and light-scattering systems,⁸⁻¹⁰⁾ we will not deal with such cases. Extension of the present analysis to viscometric monitor installed *GPC* will be straightforward. While that to light-scattering monitor installed *GPC* will be problematic, because of the complexities in light-scattering from compositionally heterogeneous copolymer solutions:¹¹⁾ The problem will be discussed in a later publication.

THEORETICAL

Compositional Heterogeneity and Molecular Weight Distribution

We consider a mixed radial teleblock copolymer which consists of several different species inducing *S*-homopolymer precursor, *SB*-block copolymer intermediates, and teleblock species of *j* branches, $(SB)_jX$ ($j=1,2,\dots,f$), which will be designated as *j*-mer. For convenience we designate the *S*-precursor as 0-mer, and *SB*-intermediates as 1-mer also, which is equivalent to $(SB)X$ except the coupling agent *X*. (We neglect the contribution of *X* to the molecular weight.) The mole fraction n_j of the *j*-mer should be derived from teleblock copolymerization mechanism or from easily accessible experimental data, as will be discussed later. We further assume that the *MWD*s of *S*- and *B*-blocks are independent of each other: An *SB*-intermediate is formed by coupling randomly chosen *S*- and *B*-blocks from their mother assemblies. This is equivalent to assume that in a living block copolymerization the active end of every *S*-precursor has an equal ability of initiating polymerization of *B*-monomers irrespective of the chain length. Then a *j*-th teleblock species is formed by coupling randomly chosen *j* pieces of such *SB*-intermediates with a coupler molecule *X*.

We first consider the heterogeneity of the *j*-th teleblock species. Let $N_K(M)dM$ ($K=S$ or B) represent the normalized number-based *MWD* of the mother assembly of the *K*-block. Then the mole fraction of a particular component having $M=M_S+M_B=(M_1+M_2+\dots+M_j)_S+(M_1+M_2+\dots+M_j)_B$ will be

$$\begin{aligned} & N_j(M_{1S}, \dots, M_{jS}; M_{1B}, \dots, M_{jB}) dM_{1S} \dots dM_{jB} \\ &= \prod_{i=1}^j N_S(M_{iS}) dM_{iS} \prod_{k=1}^j N_B(M_{kB}) dM_{kB} \end{aligned} \quad (1)$$

Writing the composition (by weight fraction of *S*) as $x=M_S/M$, and integrating over all possible combination of M_{iS} and M_{kB} under the conditions of $xM=M_{1S}+M_{2S}+\dots+M_{jS}$ and $(1-x)M=M_{1B}+M_{2B}+\dots+M_{jB}$, we have an equation for the (weight-based) *CH* and *MWD* function of the *j*-mer, $W_j(x, M) dx dM$, as follows:

$$W_j(x, M) dx dM = (M | \langle M_j \rangle_n) \int \int \dots \int \prod_{i=1}^j N_S(M_{is}) dM_{is} \int \int \dots \int \prod_{k=1}^j N_B(M_{kB}) dM_{kB} \quad (2)$$

where $\langle M_j \rangle_n$ is the number-average molecular weight of the j -mer. The two $(j-1)$ -ple integration in Eq. 2 may be carried out with an aid of a computer. However, the direct integration is inconvenient and time consuming if j is large.¹²⁾ In such cases the application of Monte Carlo method looks promising.¹³⁾ Also as an approximation, use of adequate analytical MWD function such as the Schulz MWD function¹⁴⁾ will be convenient. This will be discussed later.

Once the $W_j(x, M) dx dM$ functions are given, the CH - and MWD -function of the whole system is given as

$$W(x, M) dx dM = \sum_{j=1}^{\text{all}} w_j W_j(x, M) dx dM \quad (3)$$

where w_j is the weight fraction of the j -mer, including the S -precursor and the SB -block intermediate. Then knowledge of the $N_K(M) dM$ functions and the relative amounts of the j -mers, n_j or w_j , will suffice to predict the complete CH - and MWD -function of the mixed teleblock copolymer.

Average Quantities

Certain average quantities can be derived from Eqs. 2 and 3 even without knowing the $N_K(M) dM$ functions.⁴⁾ First we can correlate average composition \bar{x}_j (by weight fraction of S), number- and weight-average molecular weights $\langle M_j \rangle_n$ and $\langle M_j \rangle_w$ of the j -mer with those of the K -precursors, \bar{M}_n^K and \bar{M}_w^K as follows:

$$\bar{x}_j = j_S \bar{M}_n^S / \langle M_j \rangle_n \quad (4a)$$

$$\langle M_j \rangle_n = j_S \bar{M}_n^S + j_B \bar{M}_n^B \quad (4b)$$

$$\begin{aligned} \langle M_j \rangle_w = & \bar{x}_j [\bar{M}_w^S + (j_S - 1) \bar{M}_n^S] \\ & + (1 - \bar{x}_j) [\bar{M}_w^B + (j_B - 1) \bar{M}_n^B] + 2 \bar{x}_j (1 - \bar{x}_j) \langle M_j \rangle_n \end{aligned} \quad (4c)$$

where j_K is the number of K -blocks in the j -mer. For the S -precursor (the 0-mer), we have $\bar{x}_0 = 1$, $\langle M_0 \rangle_n = \bar{M}_n^S$ and $\langle M_0 \rangle_w = \bar{M}_w^S$ by definition. Since all the teleblock species are obtained by joining j identical (on the average) SB -intermediates, we have following simple relations:

$$\bar{x}_j = \bar{M}_n^S / \bar{M}_n^{SB} = \bar{x}_{SB} \quad (5a)$$

$$\langle M_j \rangle_n = j (\bar{M}_n^S + \bar{M}_n^B) = j \bar{M}_n^{SB} \quad (5b)$$

$$\langle M_j \rangle_w = \bar{M}_w^{SB} + (j - 1) \bar{M}_n^{SB} \quad (5c)$$

where \bar{x}_{SB} , \bar{M}_n^{SB} , and \bar{M}_w^{SB} are those of the SB -intermediate and the obtained from Eq. 4 by setting $j_S = j_B = 1$. Using these equations, we have following relations for average S -content \bar{x} , number- and weight-average molecular weights \bar{M}_n and \bar{M}_w of the whole mixture:

$$\bar{x} = \sum_{j=1}^{\text{all}} w_j \bar{x}_j = w_0 + (1 - w_0) \bar{x}_{SB} \quad (6a)$$

$$M_n = \sum_{j=1}^{\text{all}} n_j \langle M_j \rangle_n = n_0 M_n^S + \sum_{j=1}^f n_j (j \bar{M}_n^{SB}) \quad (6b)$$

$$M_w = \sum_{j=1}^{\text{all}} w_j \langle M_j \rangle_w = w_0 \bar{M}_w^S + (1 - w_0) \bar{M}_w^{SB} + \sum_{j=1}^f w_j (j-1) \bar{M}_n^{SB} \quad (6c)$$

$$w_j = n_j \langle M_j \rangle_n / M_n = n_j (j \bar{M}_n^{SB} / M_n) \quad (6d)$$

Using the *CH* and *MWD* function of Eq. 2 and 3, we can also easily derive an expression of light-scattering apparent molecular weight M_{app} of a mixed block copolymer.⁴⁾ The result applied to the teleblock copolymer is as follows:

$$M_{\text{app}} = M_w + 2bP + b^2Q \quad (7a)$$

$$b = (\nu_S - \nu_B) / \nu \quad (7b)$$

where ν and ν_K are the specific refractive index increments of the copolymer and the *K*-homopolymer, respectively. The quantities M_w , P , and Q are:

$$M_w = (1 + Y) M_n = [1 + \bar{x}^2 Y_S + (1 - \bar{x})^2 Y_B] M_n \quad (8a)$$

$$P = \bar{x}(1 - \bar{x}) [\bar{x} Y_S - (1 - \bar{x}) Y_B] M_n \quad (8b)$$

$$Q = \bar{x}^2 (1 - \bar{x})^2 (Y_S + Y_B) M_n \quad (8c)$$

$$1 + Y_K = M_w^K / M_n^K = \sum_{j=1}^{\text{all}} n_j j_K (j_K + \bar{Y}_K) / (\sum_{j=1}^{\text{all}} n_j j_K)^2 \quad (8d)$$

where $\bar{Y}_K = (\bar{M}_w^K / \bar{M}_n^K) - 1$ is the *MWD* index of the *K*-precursor; and M_n^K and M_w^K are number- and weight-average molecular weights, respectively, of the *K*-component and should be distinguished from those of the *K*-precursor, \bar{M}_n^K and \bar{M}_w^K . The indices, M_w / M_n , P / M_w , and Q / M_w , from light-scattering apparent molecular weight can be predicted from knowledge of only \bar{x} , \bar{Y}_K , and n_j of the teleblock copolymer mixture. The problem is to deduce n_j from copolymerization mechanism or from some other easily accessible data.

GPC Chromatogram

To construct *GPC* chromatograms from the *CH* and *MWD* function, we employ the concept of the Strasbourg universal calibration⁷⁾ and Tung's phenomenological scheme for the imperfect resolution of a *GPC* unit.^{15,16)} For deriving V_e of a particular teleblock copolymer species having x , M and j -branches, we have to estimate the intrinsic viscosity $[\eta]$ of the species. To this end we introduce two simple assumptions: One is to relate $[\eta]$ of a linear block copolymer with x and M with $[\eta]$ of the parent homopolymer with M ,¹⁷⁾ and the other is to relate $[\eta]$ of a random j -arm star molecule with that of a corresponding linear chain.¹⁸⁾ The result is

$$[\eta]_{\text{teleblock}} = g_r^{1/2} \{x[\eta]_S^{2/3} + (1-x)[\eta]_B^{2/3}\}^{3/2} \quad (9a)$$

$$g_r = 6j / (j+1)(j+2) \quad (9b)$$

Then molecular weight M_e of corresponding elution standard (which is usually *PS*) can be related with x and M of the teleblock copolymer species as

$$K_e M_e^{(1+a_e)} = g_r^{1/2} \{x K_s^{2/3} M^{2(1+a_s)/3} + (1-x) K_B^{2/3} M^{2(1+a_B)/3}\}^{3/2} \quad (10)$$

where K_R and a_R ($R=e, S$ or B) are the parameters in the Mark-Houwink viscosity equations of the elution standards, PS and PB , respectively. Using Eq. 10a and the calibration curve $V_e=f(\log M_e)$ for the elution standards, we fractionated on a computer $W(x, M) dx dM$ to construct $F(V_e) dV_e$ which is a hypothetical chromatogram obtained if the GPC has unlimited resolution. This can be easily done by using MWD function renormalized on $\log M$ scale, $\tilde{W}_j(x, M) dx d \log M = 2.303 MW_j(x, M) dx d \log M$. For homopolymer component, for example, we have

$$F(V_e) dV_e = \tilde{W}_0(M) \frac{d \log M}{d \log M_e} \frac{d \log M_e}{d V_e} dV_e \quad (11a)$$

with

$$M_e = \{(K_s/K_e)^{2/3} M^{2(1+a_s)/3}\}^{3/2(1+a_e)} \quad (11b)$$

If the elution standard is PS , $M_e=M$, and simply we have $(d \log M/d \log M_e)=1$ and $-d \log M_e/d V_e$ is the slope of the calibration curve. For j -arm teleblock copolymer species, we have

$$F(V_e) dV_e = \sum_x \tilde{W}_j(x, M) \frac{d \log M}{d \log M_e} dx \frac{-d \log M_e}{d V_e} dV_e \quad (11c)$$

where $(d \log M/d \log M_e)$ can be calculated from Eq. 10.

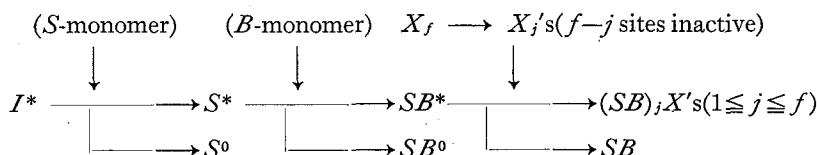
The hypothetical chromatogram $F(y) dy$ can then be converted to an actual chromatogram $G(V_e) dV_e$ by introducing Tung's band-spreading function:^{15,16)}

$$G(V_e) dV_e = \sum_y F(y) (h/\pi)^{1/2} \exp[-h(V_e-y)^2] dy dV_e \quad (12)$$

Here h is the dispersion parameter and may be determined as a function of elution volumes y for a particular GPC.^{15,16)}

Star-Branch Distribution

Usual teleblock copolymerization would follow a scheme shown below:



where* and 0 indicate active and inactive species, respectively; then I^* is active initiator and SB is excess SB -intermediates which cannot find coupling sites, and are eventually terminated before the product is recovered. If the active SB -intermediate is present in excess of the active coupling site, and if the coupling reaction could be brought to completion, the resulting branch distribution is determined solely by the distribution of active coupling sites, X'_j 's, or in other words, of the purity of the coupling agent. Then the distribution may be deduced by assuming probability of coupling sites being deactivated. However, many literatures indicate that the reactivity of a coupling site of a coupler molecule decreases as other sites are occupied by branches:¹⁹⁾ First site reacts most rapidly, second site a little slower, third one much slower, and so on. If this is the case, the

coupling reaction can hardly be brought to completion within a reasonable reaction time. In this case the branch distribution may be deduced by assuming different probabilities of the sites undergoing the coupling reaction. However, in practice such probabilities cannot be determined experimentally. Alternatively we have to devise a simple method of analyzing relative amounts of the j -mers in a given mixed teleblock sample from some easily accessible experimental data.

EXPERIMENTAL

Materials

We have examined three commercial styrene and butadiene copolymers (*SBR*) which are supposed to be radial teleblock copolymers. Their characteristics are summarized in Table I. For *GPC* calibration standards we used several Pressure Chemical polystyrenes (*PS*) (Pressure Chemical Co., Pittsburgh, U. S. A.) and a few commercial polybutadienes (*PB*) (*e. g.*, Firestone Diene 55 NFA).

Methods

These samples were subjected to *GPC* test. We employed a Shimadzu *GPC* model 1A with a bank of 10^6 , 10^5 , 10^4 , and 10^3 Å crosslinked polystyrene-gel columns (Shimadzu Seisakusho, Kyoto, Japan). The *GPC* was modified by installing, in addition to the standard refractometric (*RI*) detector, an *LKB* uv-absorption (*UV*) detector model Unicord II (*LKB* Produkter AB, Bromma, Sweden) in series between the *RI* detector and the elution dump counter. Elution solvent was tetrahydrofuran (*THF*). The flow rate was 1 ml/min. The *GPC* unit was calibrated for the band-broadening effect as well as for the

Table I. Specifications and Some Parameter Values of Radial Teleblock Copolymer Samples

Code	<i>SB2X</i>	<i>SB4X-1</i>	<i>SB4X-2</i>	
Source of Polymer	Shell Chem. Krotan 1101	Phillips Petroleum Solprene 406	Phillips Petroleum Solprene 414	
<i>St</i> -content (%)	33.0	43.6	46.2	
<i>BD</i> -microstructure ^{a)}				
% cis	35.8	44.8	49.0	
% trans	53.7	43.7	40.4	
% 1,2-vinyl	7.5	11.5	11.6	
<i>MW</i> -data: ^{b)}			(A) ^{c)}	(B) ^{c)}
$10^{-4} M_n$	8.027	12.66	8.089	8.323
$10^{-4} M_n \bar{S}(\bar{P}_S)$ for <i>PS</i>	1.785(0.074)	2.900(0.102)	...2.040(0.202)	
mole fr. of j -mer				
0 mer	0.145	0.260	0.293	0.284
1 mer	0.371	0.439	—	—
2 mer	0.484	—	0.618	0.600
3 mer	—	—	—	0.116
4 mer	—	0.301	0.089	—

a) Determined by the method of Morero *et al.*²¹⁾

b) M_n data were deduced by Eq. 6 with *PS*-values determined from the *GPC* data (uncorrected for the band-broadening effects).

c) The presence of 4-arm star molecules was assumed in (A), while 3-arm star molecules in (B).

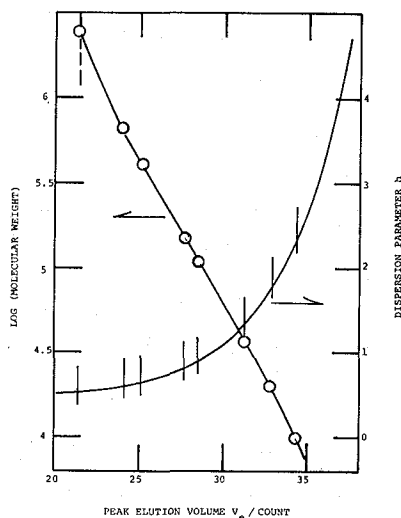


Fig. 1. Log (molecular weight) and the dispersion parameter h versus elution volume V_e for the GPC unit employed here. The calibrations were made with narrow distribution polystyrenes.¹⁶⁾

V_e versus $\log M_e$ relation, using several narrow distribution PS samples as the elution standards, by a method suggested before.¹⁶⁾ Figure 1 summarizes the two calibrations for the GPC unit employed here.

Chromatograms were analyzed according to the procedure suggested by Tung *et al.*⁶⁾ Chromatograms obtained by the UV-detector, G_{UV}' , was corrected by multiplying the ratio of response areas for standard PS in THF on the RI-detector, R_{PS} , and on the UV-detector, U_{PS} , as

$$G_{UV} = (R_{PS}/U_{PS})G_{UV}' \quad (13a)$$

where the factor on the GPC was $(R_{PS}/U_{PS}) = 0.61 \pm 0.02$. The corrected UV chromatogram, G_{UV} , reflects PS-component at each elution volume level. On the other hand, chromatogram on the RI-detector, G_{RI} , does not represent the total amount of SBR: It must be corrected for the difference in the RI-detector response to PS and PB in THF as

$$G = (G_{RI} - G_{UV})(R_{PS}/R_{PB}) + G_{UV} \quad (13b)$$

where R_{PS} and R_{PB} are the RI-response area per unit mass of PS and PB in THF, respectively, and the ratio is equal to the ratio of their specific refractive index increments, *i.e.*, $(R_{PS}/R_{PB}) = 1.36 \pm 0.02$.

The sample SB-2X was subjected to thin-layer chromatographic (TLC) analysis of compositional heterogeneity. The procedure was detailed in a previous publication,²⁰⁾ and will not be recounted here. Determination of S-content was made by UV-absorption spectrometry. Determination of butadiene microstructure was made by infrared spectrometry.²¹⁾ Other necessary characterization of the copolymer samples was carried out according to our laboratory routine,^{22,23)} and will not be repeated here.

RESULTS AND DISCUSSION

Identification of Constituent Species

Figure 2 shows corrected *RI*- and *UV*-chromatograms plotted against elution count V_e for the three teleblock samples. The figure also shows the variation of *S*-content $\langle x \rangle = G_{UV}/G$ with V_e . In these figures we see that all the samples are mixtures of a few components: In each case the component at the largest V_e region is undoubtedly homo-*PS* component (the 0-mer). From this region, \bar{M}_n^s and \bar{M}_w^s may be determined without too much difficulties. The identification of other components, however, is rather difficult, especially for the sample *SB4X-2*: Nevertheless, the assignments given in the figures and also in Table I are presumably correct, or at least, reasonable as a starting assumption.

Once the *j*-mers having been assigned, we can draw important information from the

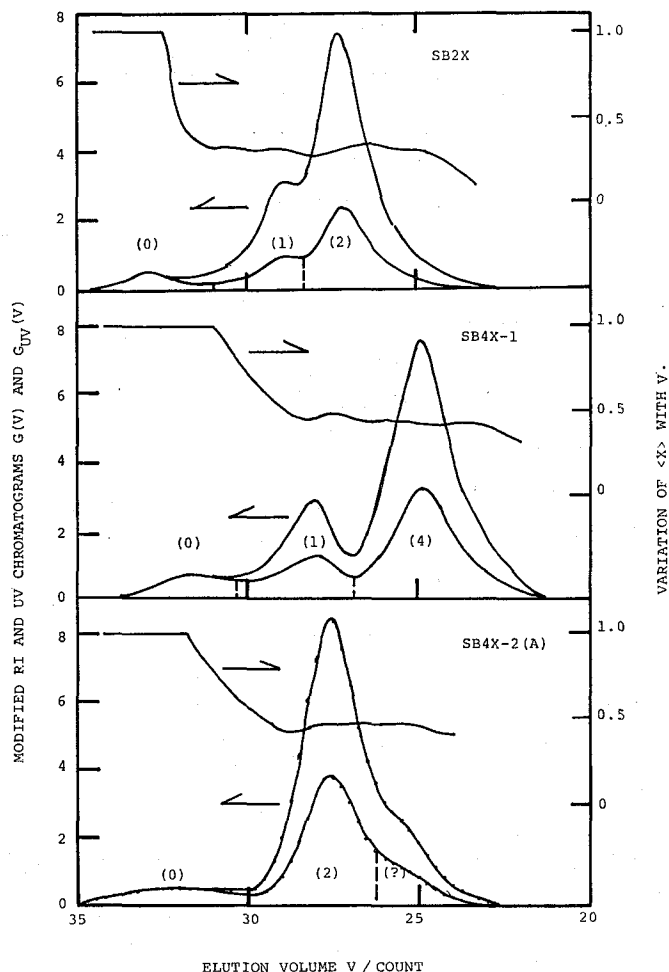


Fig. 2. Corrected *RI*- and *UV*-chromatograms together with $\langle x \rangle$ versus V_e relations of the teleblock copolymer samples. The *UV*-chromatograms were divided into the corresponding *j*-mer regions, as indicated.

chromatograms, although we do not know the detail of teleblock polymerization procedure actually employed. The area U_j of the j -mer region under the UV -chromatogram should be proportional to the amount of PS -component of the j -mer, *i.e.*,

$$U_j \propto n_j(j_S \bar{M}_n^S) \propto w_j \bar{x}_j \quad (14)$$

Although the S -regions of the adjacent j -mers usually overlap with each other, the sectioning of the area by the way such as shown in the figures would allow reasonable estimates of U_j 's for the purpose of estimating n_j 's. On the other hand, the average S -content \bar{x}

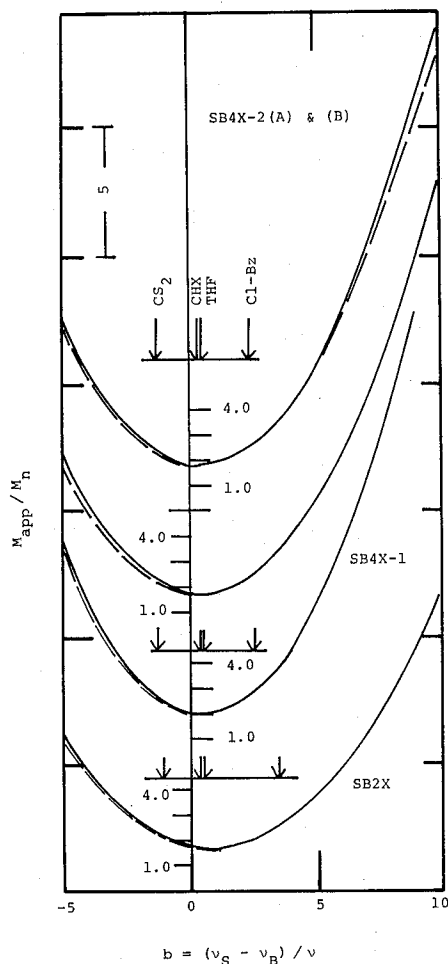


Fig. 3. Dependence of light-scattering apparent MW on solvent refractive index, plotted in the form M_{app}/M_n versus b with \bar{V}_B as an adjustable parameters. The arrows indicate the b -values in given solvents: CS_2 =carbon disulfide; CHX =cyclohexane; THF =tetrahydrofuran; and $Cl-BZ$ =chlorobenzene.

The values of n_j and \bar{V}_S employed are those listed in Tab. I, while \bar{V}_B is handled as an adjustable parameter. The values are varied from 0.404 (solid curve) to 0.101 (dashed curve) for $SB4X-2(A)$ and (B); from 0.204 to 0.068 for $SB4X-1$; and from 0.148 to 0.037 for $SB2X$. In each case solid curve is from the former value and dashed curve from the latter: The changes are very small as shown in the figure.

and the weight fraction of the S -precursor (the 0-mer) left in the system w_0 are, respectively, $\bar{x} = U/A$ and $w_0/\bar{x} = U_0/U$, where U is the total area under the UV -chromatogram and A is that under the corrected chromatogram, G versus V_e . Then from all these data with use of Eqs. 4–6 and 14, we can easily estimate the values of w_j , $\bar{x}_j (= \bar{x}_{SB}$ for $1 \leq j \leq f$), $\langle M_j \rangle_n$ and M_n .

On the other hand, estimation of $\langle M_j \rangle_w$ is somewhat problematic, because it requires the value of \bar{M}_w^B and there is no direct method of determining this quantity. One possibility is light-scattering measurement in a solvent having $\nu_s = 0$ that allows determination of M_w^B . Then we can estimate \bar{Y}_B by Eq. 8, using the values of n_j 's. Also light-scattering measurements in a variety of solvents would allow determination of M_w , P , and Q by Eq. 7, and then \bar{Y}_B by Eq. 8. Figure 3 shows M_{app} versus b plots for the three teleblock samples with using \bar{Y}_B as an adjustable parameter. Apparently the M_{app} versus b plots are not very sensitive toward the variation of \bar{Y}_B for the present systems, particularly in such solvents that have sufficiently large ν -values and hence allow reasonably accurate light-scattering measurements. Alternatively we notice that in the GPC chromatograms the S -content $\langle x \rangle$ stays constant or decreases slightly with decreasing V_e , i.e., increasing M after the initial rapid decrease of $\langle x \rangle$ from the 0-mer to the next region. This behavior is the indication that $\bar{x}_{SB} \bar{Y}_S - (1 - \bar{x}_{SB}) \bar{Y}_B$ is nearly zero or slightly negative.⁴⁾ Perhaps the choice of \bar{Y}_B in the range $[\bar{x}_{SB}/(1 - \bar{x}_{SB})] \bar{Y}_S \leq \bar{Y}_B$ would be appropriate.

CH and MWD-Functions

Calculation of $W(x, M) dx dM$ of a radial teleblock copolymer by Eqs. 2 and 3 from n_j 's and the MWD -functions of S - and B -precursors is not practical, since we usually do not know the MWD of the latter. Therefore, in this study we employed Schulz MWD -function¹⁴⁾ for the precursors:

$$W_K(M) = [y_K^{(h_K+1)} / \Gamma(h_K+1)] M^{h_K} \exp(-y_K M) dM \quad (15a)$$

$$y_K = h_K / \bar{M}_n^K = (h_K+1) / \bar{M}_w^K = (h_K+2) / \bar{M}_z^K = \dots \quad (15b)$$

where Γ is the gamma function. Then from Eqs. 2 and 14, we have the following equation for the j -mer:

$$\begin{aligned} & \tilde{W}_j(x, M) dx d \log M \\ &= 2.303 \frac{(h_S / \bar{M}_n^S)^{j_S h_S} (h_B / \bar{M}_n^B)^{j_B h_B}}{\Gamma(j_S h_S) \Gamma(j_B h_B)} \{(x)^{(j_S h_S - 1)} (1-x)^{(j_B h_B - 1)}\} \\ & (M)^{(j_S h_S + j_B h_B) + 1} \exp \{ -[(h_S / \bar{M}_n^S)x + (h_B / \bar{M}_n^B)(1-x)]M \} dx d \log M \end{aligned} \quad (15c)$$

Then we can easily calculate the CH - and MWD -function of a mixed teleblock copolymer with adequate choice of parameters such as listed in Table I. Figures 4 and 5, respectively, show the CH -functions $W(x)$ and the MWD -functions $\tilde{W}(M)$ with $\langle x \rangle$ versus M relations, which are defined as

$$W(x) dx = \int_{-\infty}^{\infty} \tilde{W}(x, M) d \log M dx \quad (16a)$$

$$\tilde{W}(M) d \log M = \int_0^1 \tilde{W}(x, M) dx d \log M \quad (16b)$$

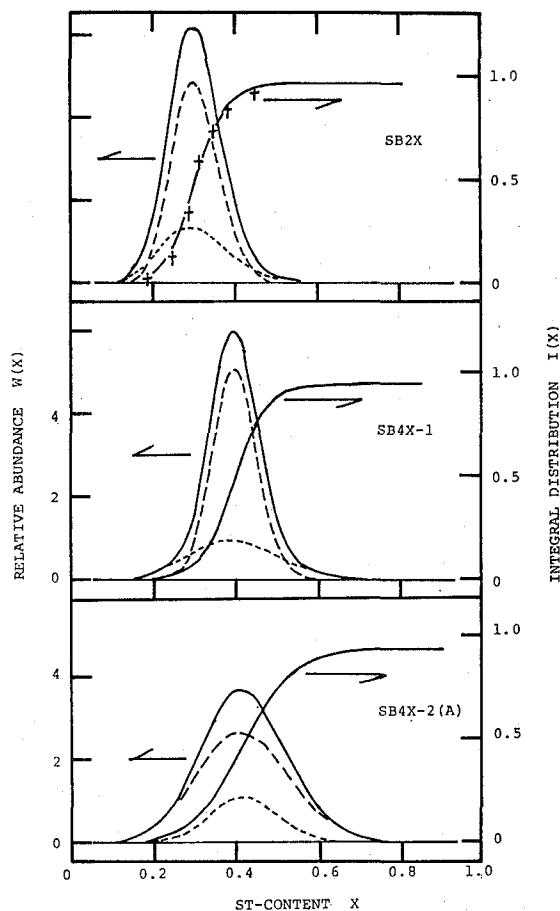


Fig. 4. Theoretical compositional heterogeneity functions, $W(X)$ versus X , for the three samples $SB2X$, $SB4X-1$, and $SB4X-2(B)$, for which the parameters listed in Tab. I were employed, and $\bar{Y}_B = \bar{Y}_S$ was assumed. For $SB2X$, TLC data are also plotted (+).

$$\langle x \rangle = \int_0^1 x \tilde{W}(x, M) dx / \int_0^1 \tilde{W}(x, M) dx \quad (16c)$$

In Fig. 4, TLC result on the sample $SB-2X^{20)}$ is compared with the present theory. The agreement seems to be reasonably good. Also the general features of the $W(M)$ curves are in agreement with those of the GPC chromatograms. A better comparison can be made by constructing GPC chromatograms from the theoretical $\tilde{W}(x, M)$ function.

Construction of GPC Chromatograms

To construct GPC chromatograms of the samples from their CH and MWD functions, we have carried out the computer simulation¹⁶⁾ based on Eqs. 9 through 12. For estimating the elution standard referred MW values, M_e , we employed Mark-Houwink equations of Iwama, Abe, and Homma²⁴⁾ for PS and PB given, respectively, as follows:

$$PS\text{-}THF, 35^\circ C \quad [\eta] = 12.3 \times 10^{-5} M^{0.703}$$

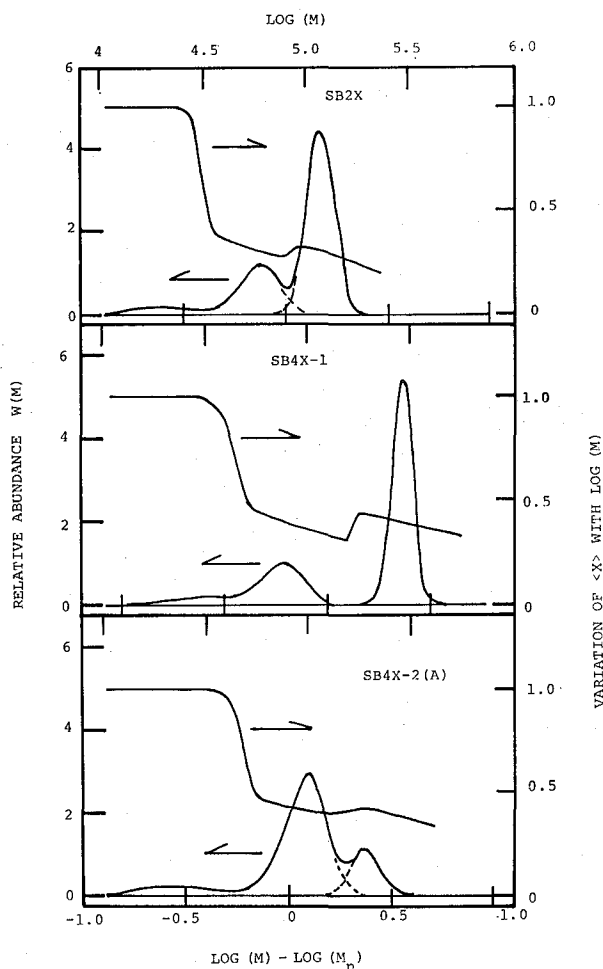


Fig. 5. Theoretical MWD functions and $\langle x \rangle$ versus $\log M$ relations for the same samples as in Fig. 4.

$$PB-THF, 35^{\circ}C \quad [\eta] = 21.2 \times 10^{-5} M^{0.739}$$

For $GPC\ MW$ versus V_e and h versus V_e calibrations, we employed the relations shown in Fig. 1, which were assigned for our particular GPC unit by the method proposed before.¹⁶⁾

Resulting chromatograms are shown in Fig. 6 together with the experimental chromatograms for the teleblock copolymer samples. In general they are qualitatively in good agreement with each other. However, a closer inspection of the experimental and theoretical chromatograms reveals certain discrepancies. For example, for the sample $SB2X$, the experimental chromatogram shows a distinct shoulder of presumably the SB -intermediate and a large tailing of the main component toward smaller elution-volume side. On the other hand, in the theoretical chromatogram the bands from the two components merge to form a single rather sharp peak with an almost imperceptible shoulder for the SB -intermediate. These discrepancies are apparently due to poor approximations employed for the sample specification on the one hand, and for the computer

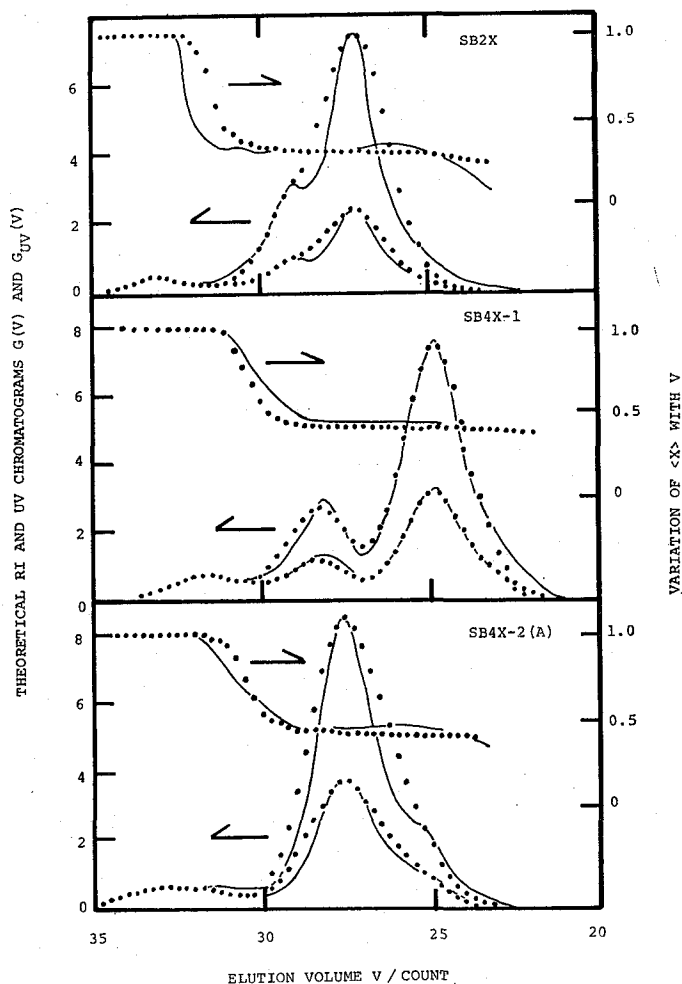


Fig. 6. Reconstructed *GPC* chromatograms (by Eqs. 9 through 12 and 15) and experimental chromatograms (replotted from Fig. 2) for the same samples as in Fig. 4.

simulation of the *GPC* fractionation on the other. First of all we do not exactly know whether the sample has the chain architecture we have postulated: The *SB*-intermediate might not be a two block *SB*-copolymer but a tapered *SB*-block copolymer. In addition we have assigned $\bar{Y}_A = \bar{Y}_B = 0.074$ (for the sample *SB2X*), employing \bar{Y}_A value, which was deduced from the *PS*-region of the chromatogram and was uncorrected for the dispersion effect. If the correction is made, the \bar{Y}_A value becomes somewhat smaller than the assigned one, and hence, the *MWDs* of the intermediate and the main component become narrower. This would lead to a more distinct shoulder for the intermediate. However, this would also lead to a much sharper peak for the main component, which showed a broader tail in the experimental chromatogram. Then, this might imply that the use of Gaussian-shape hand-spreading function¹⁵⁾ might be inadequate for correcting the effects of imperfect resolution of this particular *GPC* unit. In spite of these ambiguities, the present theory predicts reasonably good *GPC* chromatograms. Then we may hopefully

expect that the random-coupling theory of block copolymerization would provide a basis for describing the feature of the *CH* and *MWD* of radial teleblock copolymers.

One more comment should be added to the heterogeneity of the sample *SB2X* (Kraton 1101). Previous *TLC* experiments of Donkai, Miyamoto, and Inagaki²⁵) on several styrene-butadiene copolymers including the sample *SB2X* provided an evidence that the satellite component might be an *SBS* triblock component with a smaller *MW*, although the reason why such a triblock component should be there is not clear. The present analysis postulates it as an *SB* diblock component which serves as the *SB*-intermediate for the teleblock copolymerization. If this assumption is invalid, we should analyze the sample as a mixture of two *SBS* triblock components arisen from different sources.

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